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The Weight of a Falling Drop and the Laws of Tate. The Drop Weights and Molecular Weights of Some of the Lower Esters

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DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE IN COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK.

BY

FREDERICK W. SCHWARTZ

NEW YORK CITY

1911

EASTON, PA.:
ESCHENBACH PRINTING CO.
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ACKNOWLEDGMENT.

To Professor J. Livingston R. Morgan the author wishes to express his sincere thanks for advice, assistance and encouragement afforded him throughout the work. F. W. S.

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The Weight of a Falling Drop and the Laws of Tate.[1] The Drop Weights and Molecular Weights of Some of the Lower Esters.

OBJECT OF THE INVESTIGATION.

As has been shown in former researches,[2] the weight of a drop of liquid falling from a properly constructed tip is proportional, for any one diameter of tip, to the surface tension of the liquid; and further, that when falling drop weights are substituted for surface tensions in the formula of Eötvös,[3] as modified and presented by Ramsay and Shields,[4] the molecular weights and critical temperatures of liquids can be calculated with an accuracy equal to that attained by the use of the surface tensions from the capillary rise method, notwithstanding the statements of Guye and Perrot[5] to the contrary. The object of this investigation has been the testing of the new definition of normal molecular weight in the liquid state as given by Morgan and the comparison of the surface tensions and critical temperatures of some of the lower esters, determined by capillary rise and drop weight methods. The esters chosen for this investigation were methyl formate, ethyl formate, propyl formate, amyl formate, methyl acetate, ethyl acetate, propyl acetate, methyl propionate, ethyl propionate, methyl butyrate and methyl isobutyrate.

With the aid of a simple form of apparatus devised by Professor Morgan, the determination of the drop weights of

[1] Tate, *Phil. Mag.*, 4th Ser., 27, 176 (1864).

[2] Morgan and Stevenson, *Jour. Am. Chem. Soc.*, 30, No. 3; Morgan and Higgins, *Jour. Am. Chem. Soc.*, 30, No. 7.

[3] Eötvös, *Wied. Ann.*, 27.

[4] Ramsay and Shields, *Zeit. phys. Chem.*, 12, 1893.

[5] Guye and Perrot, *Arch. Sci. Phys. et Nat.*, 4 s., 11 (1901); 4 s., 15 (1903).

liquids has been rendered more simple than by the methods used by Morgan and Higgins and Morgan and Stevenson.

APPARATUS AND METHOD.

The apparatus and methods used were the same as described by Morgan.[1] The chemicals with the exception of amyl formate were manufactured especially for this investigation by the Hoffman and Kropff Chemical Company, and were exceptionally pure and gave entire satisfaction. The amyl formate was obtained from Messrs. Eimer and Amend and was purified before use.

The following symbols and abbreviations have been use throughout this work:

t = centigrade temperature.
T_c = critical temperature.
A = weight in grams of vessel plus 25 drops of liquid.
B = weight in grams of vessel plus 5 drops of liquid.
C = average weight in grams of vessel plus 25 drops of liquid.
D = average weight in grams of vessel plus 5 drops of liquid.
D. W. = weight in milligrams of one drop of liquid.
K = drop weight constant.
K′ = surface tension constant.
γ = surface tension in dynes per square centimeter.
d = density.
M = molecular weight in the liquid state.

For the calculation of K the following modified equation of Ramsay and Shields has been used.

$$K = \frac{W\left(\frac{M}{d}\right)^{\frac{2}{3}}}{T_c - (t + 6)}$$ where W = the drop weight in milligrams.

Surface tension being proportional to drop weights, as shown by Morgan the following equation was used to calculate surface tension:

$\gamma = \frac{D.W. \times K'}{K}$, from the proportion, γ : D. W. :: K′ : K.

[1] Morgan, *Jour. Am. Chem. Soc.*, 33, No. 3.

STANDARDIZATION OF TIP.

Benzene. M = 78. T_c = 288.4°.

t.	A.	B.	C.	D.	D.W.
10.0	7.6515	7.0063			
	7.6516	7.0062			
	7.6515	7.0064			
	7.6514	7.0063	7.6515	7.0063	32.26
40.7	11.0195	10.4610			
	11.0194	10.4612			
	11.0194	10.4611			
	11.0193	10.4611	11.0194	10.4611	27.915

t.	d.	D.W.	$W(\frac{M}{d})^{2/3}$.	K.	Mean K.
10.0	0.8895549	32.26	636.72	2.3374	
40.7	0.8568299	27.915	564.90	2.3372	2.3373

Pyridine. M = 79. T_c = 346.6°.

t.	A.	B.	C.	D.	D.W.
0.1	8.5643	7.6986			
	8.5642	7.6984			
	8.5643	7.6984			
	8.5644	7.6985	8.5643	7.69847	43.292
34.25	11.7086	10.9472			
	11.7084	10.9472			
	11.7085	10.9474			
	11.7087	10.9475			
	11.7088	10.9472	11.7086	10.9473	38.005

t.	d.	D.W.	$W(\frac{M}{d})^{2/3}$.	K.	Mean K.
0.1	1.0014	43.292	796.31	2.3359	
34.25	0.9672	38.005	716.58	2.3360	2.33595

The diameter of the tip was 5.53 millimeters.

The constant used throughout the work was the benzene constant 2.3373. In the standardization of the tip, only the results given by benzene were used, in order to make comparisons with the results of other observers who also used benzene as a standardizing liquid. The K used was found by use of the modified Ramsay and Shields formula using the various benzene values.

The surface tensions were all calculated from the formula as given previously, K′ being the constant given by the investigators who used the capillary rise method.

DISCUSSION OF RESULTS.

New Liquids.

In Tables 24–48 are given the $W\left(\frac{M}{d}\right)^{2/3}$ and the T_c values calculated from K in the relationship $W\left(\frac{M}{d}\right)^{2/3} = K(T_c - t - 6)$ using the molecular weights of Young and Thomas, together with the values from capillary rise. It will be remembered here that *normal molecular weight (Morgan) is shown by the attainment of the same calculated value of T_c from the equation* $W\left(\frac{M}{d}\right)^{2/3} = K(T_c - t - 6)$ *at all temperatures of observation.*

Agreement of the values of T_c from drop weight and surface tension would show then further, that D. W. : γ :: K : K′, for the molecular weight, is the same and the density is the same function of temperature in all cases. To prove the relationship D. W. : γ :: K : K′ *directly*, the values of γ are given both from drop weight and from curves in Tables 12–23.

In Tables 1–11, the experimental results are given for the esters. The agreement between the results of any one liquid at any one temperature, show that great accuracy may be attained in every case. An examination of columns, A, B, C, D, in these tables shows in some series great differences at various temperatures due to various weighing vessels used.

In Tables 12–23 are comparisons of the surface tensions by drop weight and capillary rise methods. It will be seen that remarkable agreements are obtained in nearly all cases, even in those in which the results were extrapolated far beyond the experimental points. It is to be doubted in some cases where the agreement is not very close, that the K′ for benzene from capillary rise was determined with as great accuracy as it was for the esters. This is to be especially noted in Table 14.

In Tables 16–23 the disagreement of the results of Ramsay and Aston with tubes of different radii is often greater than when compared with those results taken from the curve.

TABLE 1.—Methyl formate.

t.	A.	B.	C.	D.	D. W.
0.1	8.2323	7.6345			
	8.2323	7.6345			
	8.2325	7.6345			
	8.2324	7.6346	8.23237	7.63452	29.893
6.7	8.3898	7.8125			
	8.3898	7.8126			
	8.3897	7.8125			
	8.3897	7.8126	8.38975	7.81255	28.86
10.0	7.5554	6.9906			
	7.5553	6.9906			
	7.5554	6.9904			
	7.5555	6.9906	7.5554	6.99055	28.243
16.4	8.3485	7.8013			
	8.3486	7.8013			
	8.3485	7.8013			
	8.3484	7.8013	8.3485	7.8013	27.36
27.82	8.3071	7.7948			
	8.3072	7.7949			
	8.3071	7.7949			
	8.3073	7.7950	8.30717	7.7949	25.614

TABLE 2.—Ethyl formate.

0.1	8.1827	7.6228			
	8.1827	7.6230			
	8.1828	7.6230			
	8.1828	7.6231			
		7.6231	8.18275	7.6229	27.993
6.0	8.3243	7.7809			
	8.3243	7.7810			
	8.3242	7.7808			
	8.3244	7.7809	8.3243	7.7809	27.17
10.0	8.3355	7.8028			
	8.3358	7.8030			
	8.3357	7.8029			
	8.3357	7.8030	8.33567	7.80292	26.638
17.0	8.2888	7.7751			
	8.2886	7.7752			
	8.2889	7.7753			
	8.2889	7.7752	8.2888	7.7752	25.68
33.95	10.9059	10.4381			
	10.9058	10.4382			
	10.9059	10.4380			
	10.9060	10.4383	10.9059	10.43815	23.388

TABLE 3.—Propyl formate.

t.	A.	B.	C.	D.	D. W.
0.1	7.5616	6.9895			
	7.5615	6.9895			
	7.5615	6.9894			
	7.5615	6.9894	7.56152	6.98945	28.604
5.4	8.3638	7.8050			
	8.3639	7.8050			
	8.3638	7.8050			
	8.3638	7.8050	8.36382	7.8050	27.941
10.0	8.3492	7.8026			
	8.3494	7.8027			
	8.3494	7.8027			
	8.3494	7.8025	8.34935	7.80262	27.337
17.0	8.3283	7.7992			
	8.3284	7.7992			
	8.3284	7.7992			
	8.3283	7.7992	8.32835	7.7992	26.458
34.75	7.4595	6.9733			
	7.4593	6.9735			
	7.4594	6.9736			
	7.4595	6.9735	7.45942	6.97347	24.298
60.3	7.3903	6.9620			
	7.3903	6.9619			
	7.3902	6.9619			
	7.3905	6.9619			
	7.3902		7.3903	6.96192	21.419

TABLE 4.—Amyl formate.

10.0	8.3484	7.7993			
	8.3486	7.7992			
	8.3485	7.7992			
	8.3485	7.7992	8.3485	7.79922	27.464
35.0	8.2813	7.7875			
	8.2813	7.7875			
	8.2814	7.7875			
	8.2812	7.7875	8.2813	7.7875	24.69
60.1	8.2176	7.7796			
	8.2176	7.7796			
	8.2177	7.7797			
	8.2177	7.7795			
	8.2177		8.21767	7.7796	21.904

TABLE 5.—Methyl acetate.

	A.	B.	C.	D.	D. W.
0.1	8.2152	7.6292			
	8.2151	7.6291			
	8.2150	7.6291			
	8.2152	7.6290	8.21512	7.6291	29.301
10.0	6.8070	6.2510			
	6.8069	6.2509			
	6.8068	6.2508			
	6.8068	6.2507	6.80687	6.25085	27.801
34.20	8.2822	7.7990			
	8.2823	7.7991			
	8.2822	7.7991			
	8.2824	7.7991	8.28227	7.79907	24.16

TABLE 6.—Ethyl acetate.

0.1	7.5421	6.9834			
	7.5420	6.9834			
	7.5421	6.9832			
	7.5422	6.9832	7.5421	6.9833	27.94
34.60	7.4442	6.9767			
	7.4443	6.9768			
	7.4443	6.9767			
	7.4442	6.9769			
	7.4442	6.9766	7.44424	6.97674	23.375
60.5	7.3658	6.9646			
	7.3659	6.9647			
	7.3659	6.9646			
	7.3660	6.9646	7.3659	6.96462	20.064

TABLE 7.—Propyl acetate.

0.1	8.1884	7.6199			
	8.1885	7.6198			
	8.1886	7.6199			
	8.1887	7.6200	8.18855	7.6199	28.433
34.60	7.4602	6.9773			
	7.4603	6.9773			
	7.4602	6.9772			
	7.4602	6.9773	7.46022	6.97727	24.148
60.1	11.1213	10.6972			
	11.1216	10.6973			
	11.1215	10.6974			
	11.1215	10.6974	11.12147	10.69732	21.208

TABLE 8.—Methyl propionate.

t.	A.	B.	C.	D.	D. W.
10.0	6.8100	6.2513			
	6.8102	6.2513			
	6.8100	6.2512			
	6.8101	6.2510	6.81007	6.2512	27.944
34.65	0.9364	10.4426			
	10.9362	10.4425			
	10.9363	10.4425			
	10.9363	10.4427	10.9363	10.44257	24.687
59.75	10.8000	10.3701			
	10.8002	10.3703			
	10.8002	10.3702			
	10.8001	10.3699	10.8001	10.37012	21.499
	10.8000				

TABLE 9.—Ethyl propionate.

10.0	6.7887	6.2480			
	6.7888	6.2480			
	6.7888	6.2478			
	6.7887	6.2478	6.78875	6.2479	27.043
33.89	9.8185	9.3356			
	9.8187	9.3356			
	9.8186	9.3355			
	9.8186	9.3356	9.8186	9.33557	24.152
59.15	10.7920	10.3682			
	10.7921	10.3682			
	10.7920	10.3681			
	10.7919	10.3680	10.7920	10.36812	21.194

TABLE 10.—Methyl isobutyrate.

10.0	9.8776	9.3452			
	9.8775	9.3450			
	9.8773	9.3451			
	9.8776	9.3452	9.8775	9.34512	26.619
33.87	9.8085	9.3336			
	9.8084	9.3337			
	9.8083	9.3335			
	9.8083	9.3338			
	9.8087	9.3338	9.80845	9.33366	23.740
60.1	9.7385	9.3260			
	9.7386	9.3261			
	9.7387	9.3259			
	9.7387	9.3259			
		9.3259	9.73862	9.32594	20.634

TABLE 11.—Methyl butyrate.

t.	A.	B.	C.	D.	D.W.
10.0	8.3627	7.8043			
	8.3626	7.8042			
	8.3627	7.8042			
	8.3625	7.8042	8.36262	7.80422	27.92
34.8	8.2869	7.7885			
	8.2867	7.7885			
	8.2868	7.7885			
	8.2868	7.7885	8.2868	7.7885	24.915
59.85	8.2217	7.7824			
	8.2218	7.7824			
	8.2217	7.7824			
	8.2216	7.7824	8.22168	7.7824	21.964
	8.2216				

SURFACE TENSION.

TABLE 12.—Methyl formate.

t.	γ R. & S.[1].	γ.	From curve S.	$\left(w \frac{2.1012}{2.3373}\right)$
20.0	24.64	24.11		
30.0	23.09	22.72*		
40.0	21.56	21.34*		
50.0	20.05	19.95*		
60.0	18.58	18.57*		
70.0	17.15	17.19*		

TABLE 13.—Amyl formate.

t.	γ H. & G.[2]	γ.	From curve S.	$\left(w \frac{2.1012}{2.3373}\right)$
43.8	21.64	21.51		
77.8	18.40	18.12*		
109.2	15.52	15.05*		

[1] Ramsay and Shields, *Zeit. phys. Chem.*, 1893.

[2] Homfray and Guye, *Jour. de Chem. Phys.*, 1903, 1.

TABLE 14.—Ethyl acetate.

$t.$	$\gamma.$		$\gamma.$ From curve S. $\left(w \frac{2.106}{2.3373}\right)^{\mp}$
9.5	24.71	G. & B.[1]	24.05
12.9	24.14	R. & G.[2]	23.74
20.0	23.60	R. & S.	22.82
31.3	21.87	R. & G.	21.43
46.9	20.11	R. & G.	19.63
55.0	19.06	R. & G.	18.70
55.6	18.82	G. & B.	18.63
65.9	17.76	R. & G.	17.45*
73.5	17.07	R. & G.	16.57*
77.0	16.63	G. & B.	16.17*
80.0	16.32	R. & S.	15.83*
90.0	15.14	R. & S.	14.67*
100.0	13.98	R. & S.	13.53*

TABLE 15.—Methyl isobutyrate.

$t.$	γ R. & G.	$\gamma.$	From curve S. $\left(w \frac{2.1108}{2.3373}\right)$
10.5	24.06	24.03	
30.5	21.82	21.81	
41.0	20.63	20.68	
55.0	19.18	19.18	
75.0	17.02	17.04*	
86.6	15.78	15.80*	

TABLE 16.—Ethyl formate.

	r = 0.01843 cm.		r = 0.01046 cm.
$t.$	γ R. & A.[3]	γ R & A.	γ from curve S.
10.0	24.08	24.22	24.18
46.5	19.50	19.71	19.68*
78.5	15.68	15.68	15.73*

TABLE 17.—Methyl acetate.

	r = 0.01843 cm.		r = 0.01046 cm.
$t.$	γ R. & A.	γ R. & A.	γ from curve S.
10.0	25.22	25.06	25.23
46.2	20.32	20.49	20.29*
78.3	16.28	16.35	15.89*

[1] Guye and Baud, *Arch. des Sci. Phys. et Nat.*, 4 s., Vol. 11.

[2] Renard and Guye, *Jour. de Chem. Phys.*, 1907, 5.

[3] Ramsay and Aston, *Zeit. phys. Chem.*, 15 (1894), Part 1.

*All values thus marked were extrapolated beyond points on curve.

$\mp$ K = 2.106 being a mean of R. & S. and R. & G.

TABLE 18.—Propyl formate.

	r = 0.01843 cm.	r = 0.01046 cm.	
t.	γ R. & A.	γ R. & A.	γ from curve S.
10.0	25.02	25.06	24.81
46.2	20.67	20.71	20.83
78.2	17.52	17.44	17.61*

TABLE 19.—Methyl propionate.

	r = 0.01708 cm.	r = 0.01046 cm.	
t.	γ R. & A.	γ R & A.	γ from curve S.
10.0	25.23	25.51	25.36
46.2	20.85	20.98	21.08
78.2	17.11	17.26	17.30*

TABLE 20.—Propyl acetate.

	r = 0.01708 cm.	r = 0.01046 cm.	
t.	γ R. & A.	γ R. & A.	γ from curve S.
10.0	24.00	24.88	24.69
46.2	20.86	20.84	20.71
78.2	17.35	17.41	17.36*

TABLE 21.—Ethyl propionate.

	r = 0.01708 cm.	r = 0.01046 cm.	
t.	γ R. & A.	γ R. & A.	γ from curve S.
10.0	24.57	24.57	24.54
46.2	20.58	20.62	20.60
78.2	17.24	17.22	17.20*

TABLE 22.—Methyl isobutyrate.

	r = 0.01708 cm.	r = 0.01046 cm.	
t.	γ R. & A.	γ R. & A.	γ from curve S.
10.0	24.11	24.08	24.16
46.2	20.29	20.04	20.22
78.2	16.70	16.64	16.78*

TABLE 23.—Methyl butyrate.

	r = 0.01843 cm.	r = 0.01046 cm.	
t.	γ R. & A.	γ R. & A.	γ from curve S.
10.0	25.63	25.50	25.34
46.2	21.50	21.39	21.40
78.2	18.15	18.05	17.98*

*All values thus marked were extrapolated beyond points on curve.

In Tables 24–29 are given the critical temperatures of various investigators using the K as indicated in the tables. It is rather difficult to compare directly these results with those obtained by the drop weight method.

In Tables 25–27 with ethyl acetate it may be seen that the results agree well although differences in temperature are considerable.

Comparing Table 24 with Table 38 (methyl formate) it will be noticed that the critical temperatures do not agree as well as might be expected, but this may be well explained by polymerization at the higher temperatures.

In Tables 25–27 and 43 (ethyl acetate) the results in 43 show a closer agreement with those of Young than with those of other workers.

In Tables 29 and 41 (amyl formate) the results in 41 also show a closer agreement with those determined experimentally.

In Tables 30–37 the differences between the critical temperatures determined with different tubes are quite noticeable, while with Tables 39, 40, 42–48 will show very good agreement.

From these agreements of critical temperatures calculated in Tables 38–48 it may be stated that a liquid which will give the same critical temperature at various experimental temperatures has normal molecular weight. Those liquids which do not, are either associated or as in this case decomposed at the higher temperatures. After working for some time with the formates, it became quite evident that an explanation was necessary, in view of the non-concordant results that were obtained, there being a general trend in the calculated critical temperatures with variation of temperature. It was decided to investigate the effect of heat on several of the formates, those chosen being propyl and amyl formate.

Propyl formate was heated for two and one-half hours at 60° under atmospheric pressure and allowed to cool slowly to room temperature.

Unheated sample gave drop weight at 10.0° = 27.337.

Heated sample gave drop weight at 10.0° = 27.434 determined immediately.

Heated sample gave drop weight at 10.0° = 27.430 after 16 hours.

Heated sample gave drop weight at 10.0° = 27.366 after 10 days.

Another sample was heated similarly and cooled suddenly to 0.0° and the drop weight immediately determined which gave 27.337.

These results show that some change had taken place which was apparently reversible and which is influenced largely by time and temperature.

Amyl formate was heated to 230° in a sealed tube with a small amount of mercury for three and three-fourths hours. On opening the thoroughly cooled tube considerable pressure was noticed.

Unheated sample gave drop weight at 10.0° = 27.464.

Heated sample gave drop weight at 10.0° = 27.309.

In both cases a decided differences of odor was noticed between the heated and unheated samples. As an explanation for this variation it may be assumed to be due to polymerization for lack of more confirmatory evidence. Polymerization at higher temperatures has been noticed by Young and Thomas[1] in the case of the formates and by Homfray and Guye[2] with liquids such as ethyl lactate. However Smiles[3] states "it is doubtful that the effect of temperature is related to the chemical constitution of the liquid." The formates, then may be classed as the exceptions to the statement of Gossart[4] "that the temperature coefficient is the same for substances of the same class," although his measurements deal only with the alcohols, acids, esters and some chlorine derivatives.

CRITICAL TEMPERATURE.

The following were calculated from the results of Ramsay and Shields[5] using K = 2.1012.

[1] Young and Thomas, *Trans. Chem. Soc.*, 1893.

[2] Homfray and Guye, *Jour. de Chem. Phys.*, 1903, 1.

[3] Smiles, Text-book, relations between chem. constitution and some physical properties, 1910.

[4] Gossart, *Ann. chim. phys.*, [6] 19173 (1890).

[5] Ramsay and Shields, *Zeit. phys. Chem.*, 1893.

TABLE 24.—Methyl formate.

t.	$r(\frac{M}{d})^{2/3}$	T_c.
20.0	383.9	208.70
30.0	363.7	209.09
40.0	343.2	209.33
50.0	322.6	209.53
60.0	302.5	209.96
70.0	282.7	210.54
190.0	37.7	213.94
200.0	19.2	215.13
211.0	4.0	217.89

TABLE 25.—Ethyl acetate.

20.0	500.7	264.29
80.0	367.2	260.75
90.0	344.4	259.90
100.0	321.7	259.10
110.0	299.0	258.29
120.0	277.1	257.87
245.0	7.2	254.42

The following were calculated from the results of Guye and Baud[1] using K = 2.1012.

TABLE 26.—Ethyl acetate.

t.	$r(\frac{M}{d})^{2/3}$.	T_c.
9.5	519.6	262.78
55.6	413.0	258.15
77.0	373.0	260.51

The following were calculated from the results of Renard and Guye[2] using K = 2.1108.

TABLE 27.—Ethyl acetate.

t.	$r(\frac{M}{d})^{2/3}$.	T_c.
12.0	509.0	260.04
31.3	470.0	259.96
46.9	437.0	259.93
55.0	418.0	259.02
65.9	394.0	258.55
73.5	381.0	259.99

[1] Guye and Baud, *Arch. Sci. Phys. et Nat.*, 4 s., Vol. 11.

[2] Renard and Guye, *Jour. Chimie Physique*, 5, 1907.

TABLE 28.—Methyl isobutyrate.

$t.$	$r(\frac{M}{d})^{2/3}$.	$T_c.$
10.5	563.0	283.22
30.5	519.0	282.37
41.0	496.0	281.98
55.0	467.0	282.24
75.0	422.0	280.95
86.6	396.0	280.25

The following were calculated from the results of Homfray and Guye[1] using K = 2.1012.

TABLE 29.—Amyl formate.

$t.$	$r(\frac{M}{d})^{2/3}$.	$T_c.$
43.8	569.5	320.83
77.8	497.8	320.71
109.2	432.2	320.89

The following were calculated from the results of Ramsay and Aston[2] using K = 2.1212.

TABLE 30.—Ethyl formate.

	r = 0.01843 cm.		r = 0.01046 cm.	
$t.$	$r(\frac{M}{d})^{2/3}$.	$T_c.$	$r(\frac{M}{d})^{2/3}$.	$T_c.$
10.0	443.5	225.07	446.0	226.25
46.5	371.5	227.63	375.5	227.51
78.5	309.2	230.17	309.1	230.22

TABLE 31.—Methyl acetate.

	r = 0.01843 cm.		r = 0.01046 cm.	
10.0	462.8	234.17	459.9	232.90
46.2	383.9	233.17	387.2	234.53
78.3	318.2	234.30	319.5	234.91

TABLE 32.—Propyl formate.

	r = 0.01843 cm.		r = 0.01046 cm.	
10.0	523.6	262.83	524.4	263.21
46.2	446.3	262.59	447.1	262.97
78.3	387.0	266.64	385.2	265.79

[1] Homfray and Guye, *Jour. de Chem. Phys.*, 1903, 1.

[2] Ramsay and Aston, *Jour. Chem. Soc. Trans.*, 65, 1894.

TABLE 33.—Methyl propionate.

	r = 0.01708 cm.		r = 0.01046 cm.	
10.0	524.3	263.16	530.2	265.95
46.2	447.3	263.07	450.2	264.39
78.2	378.8	262.77	381.9	264.28

TABLE 34.—Propyl acetate.

	r = 0.01708 cm.		r = 0.01046 cm.	
t.	$r(\frac{M}{d})^{2/3}$.	T_c	$r(\frac{M}{d})^{2/3}$.	T_c.
10.0	580.2	289.52	582.0	290.34
46.2	503.0	289.32	502.2	288.94
78.2	431.0	287.38	432.3	287.99

TABLE 35.—Ethyl propionate.

	r = 0.01708 cm.		r = 0.01046 cm.	
10.0	574.0	286.59	576.2	287.63
46.2	496.1	286.07	496.9	286.44
78.2	428.1	286.01	427.8	285.87

TABLE 36.—Methyl isobutyrate.

	r = 0.01708 cm.		r = 0.01046 cm.	
10.0	563.6	281.69	563.0	281.41
46.2	487.3	281.92	486.1	281.30
78.2	415.0	279.84	415.1	279.88

TABLE 37.—Methyl butyrate.

	r = 0.01843 cm.		r = 0.01046 cm.	
10.0	595.0	296.50	591.7	294.94
46.2	514.5	294.74	511.8	293.47
78.2	446.9	294.88	444.4	293.70

TABLE 38.—Methyl formate.

M = 59.86. T_c = 214° Young.[1] $\gamma = w\left(\frac{2.1012}{2.3373}\right)$

t.	D. W.	d.	$w(\frac{M}{d})^{2/3}$.	T_c.	γ.
0.1	29.893	1.00300	456.50	201.41	26.873
6.7	28.86	0.99354	443.53	202.46	25.945
10.0	28.243	0.98892	435.39	202.27	25.390
16.4	27.36	0.97943	424.51	204.02	24.596
27.82	25.614	0.96320	401.86	205.75	23.027

[1] S. Young, *Sci. Proc. Roy. Dub. Soc.*, 12, p. 374.

TABLE 39.—Ethyl formate.

$M = 73.83$. $T_c = 235.3°$ Young. $\gamma = w\left(\frac{2.1212}{2.3373}\right)$

$t.$	D. W.	$d.$	$w\left(\frac{M}{d}\right)^{2/3}$	$T_c.$	$\gamma.$
0.1	27.993	0.94697	510.86	224.66	25.401
6.0	27.17	0.93958	499.59	225.25	24.658
10.0	26.638	0.93458	490.42	225.82	24.175
17.0	25.68	0.92618	475.64	226.50	23.306
33.95	23.388	0.90418	440.18	228.27	21.226

TABLE 40.—Propyl formate.

$M = 87.8$. $T_c = 264.85°$ Young. $\gamma = w\left(\frac{2.1212}{2.3373}\right)$

0.1	28.604	0.92850	593.69	260.10	25.960
5.4	27.941	0.92251	582.44	260.59	25.358
10.0	27.337	0.91726	572.01	260.72	24.809
17.0	26.458	0.90909	556.93	261.27	24.012
34.75	24.298	0.88873	519.25	262.90	22.051
60.3	21.419	0.85837	468.46	266.72	19.439

TABLE 41.—Amyl formate.

$M = 116.1$ $T_c = 304.6°$ Palewski.[1] $\gamma = w\left(\frac{2.1012}{2.3373}\right)$

10.0	27.464	0.8882	706.26	318.60	24.686
35.0	24.69	0.8682	645.73	317.30	22.199
60.1	21.904	0.8420	584.62	316.20	19.691

TABLE 42.—Methyl acetate.

$M = 73.83$. $T_c = 233.7°$ Young. $\gamma = w\left(\frac{2.1212}{2.3373}\right)$

0.1	29.301	0.95900	530.26	232.96	26.592
10.0	27.801	0.94652	507.53	233.13	25.231
34.20	24.16	0.91491	451.16	233.22	21.926

TABLE 43.—Ethyl acetate.*

$M = 87.8$. $T_c = 250.1°$ Young. $\gamma = w\left(\frac{2.1212}{2.3373}\right)$

0.1	27.94	0.92421	581.71	254.97	25.175
34.6	23.375	0.88277	501.68	255.23	21.062
60.5	20.064	0.85019	441.63	255.44	18.078

[1] Palewski, *Ber. Chem. Ges.*, 15, 1882, p. 2463. His results are probably for the same ester as was used in this investigation.

*K used for calculation of γ was 2.106, being the mean of that of R. & S. and R. & G.

TABLE 44.—Propyl acetate.

$M = 101.77$. $T_c = 276.2°$ Young. $\gamma = w\left(\frac{2.1212}{2.3373}\right)$

$t.$	D. W.	$d.$	$w\left(\frac{M}{d}\right)^{2/3}$.	$T_c.$	$\gamma.$
0.1	28.433	0.91000	659.98	288.47	25.804
34.6	24.148	0.87229	576.55	287.32	21.914
60.1	21.208	0.84345	517.83	287.74	19.246

TABLE 45.—Methyl propionate.

$M = 87.8$. $T_c = 257.4°$ Young. $\gamma = w\left(\frac{2.1212}{2.3373}\right)$

10.0	27.944	0.92678	580.70	264.44	25.360
34.65	24.687	0.89758	524.08	264.87	22.405
59.75	21.499	0.86682	467.11	264.59	19.511

TABLE 46.—Ethyl propionate.

$M = 101.77$. $T_c = 272.9°$ Young. $\gamma = w\left(\frac{2.1212}{2.3373}\right)$

10.0	27.043	0.90106	631.86	286.32	24.543
33.89	24.152	0.87435	575.74	286.21	21.919
59.15	21.194	0.84502	516.87	286.28	19.234

TABLE 47.—Methyl isobutyrate.

$M = 101.77$. $T_c = 267.55°$ Young. $\gamma = w\left(\frac{2.1212}{2.3373}\right)$

10.0	26.619	0.90033	622.30	282.24	24.158
33.87	23.740	0.87328	566.39	282.19	21.545
60.1	20.634	0.84295	504.03	281.74	18.726

TABLE 48.—Methyl butyrate.

$M = 101.77$. $T_c = 281.3°$ Young. $\gamma = w\left(\frac{2.1212}{2.3373}\right)$

10.0	27.92	0.90925	648.44	293.42	25.338
34.8	24.915	0.88175	590.62	293.68	22.610
59.85	21.964	0.85375	531.99	293.45	19.932

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SUMMARY.

As a result of this investigation we have shown:

1. That the drop weight method, in connection with the new definition of normal molecular weight of Morgan, is the most accurate method known for the determination of molecular weight in the liquid state.

2. That the surface tension of a liquid may be most easily and exactly calculated by this method, and that a knowledge of density of the liquid is unnecessary, a factor which may be responsible for some of the poor results which are found in the literature.

3. That the definition of normal molecular weight in the liquid state, *i. e.*, such a liquid that it will give the same value of T_c at all temperatures of observation, shows that all the above liquids with the exception of the formates, are non-associated, *i. e.*, normal in molecular weight, and that the formates undergo a reversible reaction at higher temperatures, which makes them appear abnormal.

BIOGRAPHY.

Frederick William Schwartz was born in Albany, N. Y., September 2, 1883. He entered the Rensselaer Polytechnic Institute at Troy, N. Y., in 1901, and graduated in 1905 with the degree of B.S. He attended Columbia University during the summers of 1908, 1909, 1910 and also from September, 1910. Since graduation from Rensselaer he has been assistant in chemistry at Rensselaer.

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